Development of Environmental Friendly Non-Anhydride No-Flow Underfills

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***Abstract*—Most no-flow underfill materials are based on epoxy/anhydride chemistry. Due to the sensitizing nature, the use of anhydride is limited and there is a need for a no-flow underfill using nonanhydride curing system. This paper presents the development of novel no-flow underfill materials based on epoxy/phenolic resin system. Epoxy and phenolic resins of different structures are evaluated in terms of their curing behavior, thermo-mechanical properties, viscosity, adhesion toward passivation, moisture absorption and the reliability in flip-chip underfill package. The influence of chemical structure and the crosslinking density of the resin on the material properties is investigated. The assembly with nonanhydride underfill shows high reliability from the thermal shock test. Solder wetting test has confirmed the sufficient fluxing capability of phenolic resins. Results show that epoxy/phenolic system has great potential for an environmental friendly and highly reliable no-flow underfill.**

***Index Terms*—Epoxy/phenolic resin, fluxing capability, material properties, no-flow underfill, thermal shock test.**

I. Introduction

With the rapid advances in flip-chip on organic board technology, underfill becomes the key to a successful package [1]. Unlike the conventional underfill that depends on the capillary force to draw the underfill into the gap between the chip and the substrate after solder joints are formed, no-flow underfill is dispensed onto the substrate before the placement of the chip. Then the chip is placed onto the substrate and the whole assembly is subject to solder reflow when no-flow underfill can act as a fluxing agent to remove the solder oxide and prevent the solder from reoxidation. The chemistry of the no-flow underfill is so designed that the material does not gel before the solder joints are formed. No-flow underfill has the potential advantages over the conventional underfill due to its simplicity in process and has been adopted and developed for a high-speed, low-cost flip-chip process [2].

However, current underfill has relied on epoxy/anhydride chemistry. Due to their sensitizing nature, the anhydrides are limited in use by the National Board of Occupational Safety and Health in Sweden. According to the Provisions on Occupational Exposure Limit Values, several anhydrides, including hexahydrophthatlic anhydride, methyl hexahydrophthalic anhydride, methyl tetrahydrophthalic anhydride, and tetrahydrophthalic anhydride, are considered highly sensitizing and they may only be handled by permission of the Labour Inspectorate [3]. Most anhydrides have high vapor pressures and low boiling points. During the underfill curing process, the vaporization of anhydride into the atmosphere imposes environmental threat. This becomes a more serious problem regarding no-flow underfill, whose process temperature is typically higher than that of the conventional underfill. With the increasing concerns for green industry and products, there is a need for an environmental friendly no-flow underfill using nonanhydride curing system. Phenolic resins have been used as the hardener for epoxy resins in molding compound for a long time [4]. Epoxy/phenolic resins has a variety of desirable properties including excellent insulation, good adhesion, outstanding chemical resistance, and low moisture absoprtion, etc. [5]. Phenolic resins, usually solid at room temperature, are seldom used in the underfill applications where low viscosity is essential for fast flow in the capillary dispensing of the underfill. The invention of no-flow underfill elimintates the capillary flow process and allows resins with relatively higher viscosity to be applied. In the current study, semi-liquid and liquid phenolic resins are investigated as the potential hardeners for epoxy in the application of no-flow underfill. Different epoxy resins are used to achieve lower viscosity of the underfill and better properties of cured resins. Tetraphenylphosphonium tetraphenylborate is one of the common catalysts for epoxy/phenolic reactions [6] and is used in the study here.

High yield and high reliability are two major characters of a successful no-flow underfill process. Latent curing behavior and sufficient fluxing capability are necessary to achieve high yield in process, while material properties, e.g., glass transition temperature, coefficient of thermal expansion (CTE), modulus, adhesion, etc., are essential for high reliability of a package. In the current study, these properties are investigated to evaluate the epoxy/phenolic system for no-flow underfill applications.

II. Experimental

A. Materials

The formulations studied in this work were composed of epoxy resins, phenolic hardners, and a latent catalyst. Fig. 1 shows the chemical structures of all the ingredients. EP-A is poly (bisphenol A-co-epichlorohydrin), glycidyl end-capped, mentioned also as BisA epoxy resin, commonly used in the industry. EP-B is N,N-Diglycidyl-4-glycidyloxyaniline, a tri-functional epoxy with very low viscosity. EP-C is a low viscosity BisA and BisF resin mixture. EP-D is a naphthalene type epoxy solid resin at room temperature. But it has low melt viscosity at elevated temperature. PH-A through PH-D are

Manuscript received June 15, 2001; revised November 1, 2001. This work was recommended for publication by Associate Editor R. Chanchani upon evaluation of the reviewers' comments.

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Publisher Item Identifier S 1521-3331(02)02306-1.

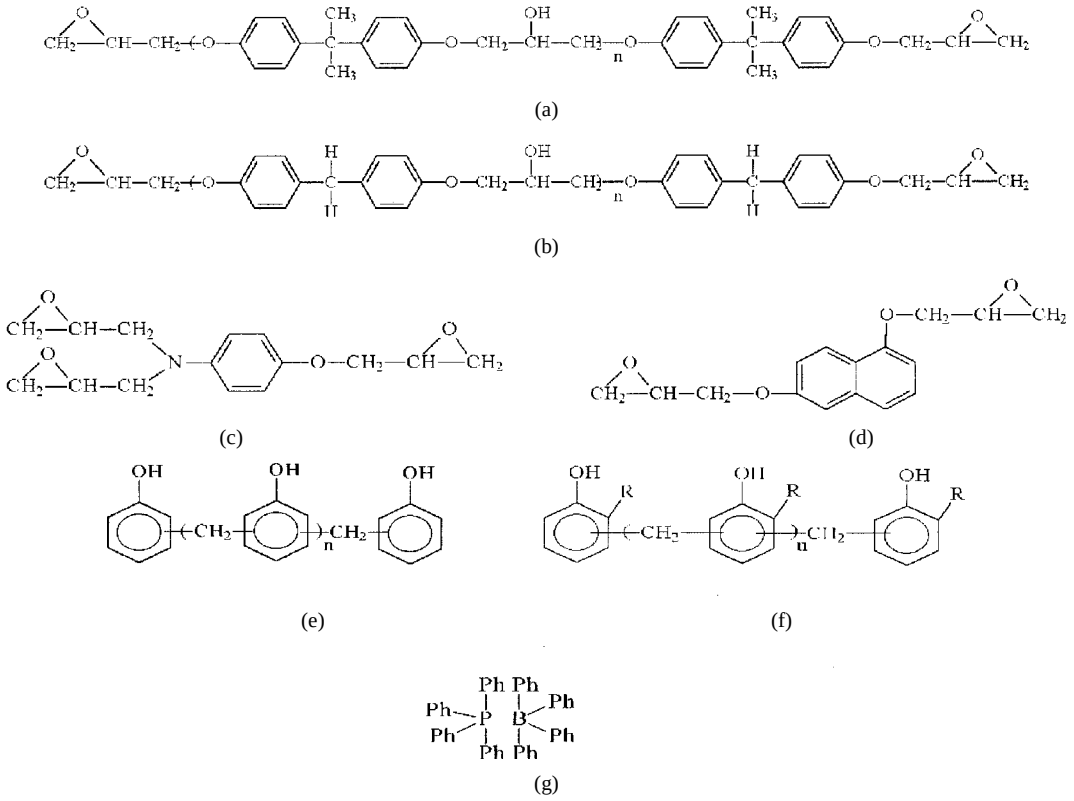


Fig. 1. Chemical structures of the ingredients used in the study: (a) BisA resin, (b) BisF resin, (c) EP-B, (d) EP-D, (e) PH-A and PH-B, (f) PH-C and PH-D, and (g) TPTB.

TABLE I
CHEMICALS USED IN THE STUDY

Epoxy resins	EP-A	EEW 188 g/eq	Aldrich Chemical Company
	EP-B	EEW 95 g/eq	Sumitomo Plastics America, Inc
	EP-C	EEW 170 g/eq	Sumitomo Plastics America, Inc
	EP-D	EEW 141 g/eq	DIC
Hardeners	PH-A	HEW 100 g/eq	Sumitomo Plastics America, Inc
	PH-B	HEW 102 g/eq	Sumitomo Plastics America, Inc
	PH-C	HEW 141 g/eq	Sumitomo Plastics America, Inc
	PH-D	HEW 135 g/eq	Sumitomo Plastics America, Inc
	HMPA	HEW 168 g/eq	Aldrich Chemical Company
Catalyst	TPTB		TCI

phenolic hardeners provided by Sumitomo Plastics America, Inc. PH-A and PH-B are semi-solid novolac type phenolic resins, the structure of which is shown in Fig. 1. PH-A has more repeat units than PH-B. PH-C and PH-D are liquid ortho-substituted phenolic resins. PH-C has more repeat units than PH-D. Methyl hexahydrophthalic anhydride (HMPA) is used as hardener for epoxy resins for comparison in the study. The epoxide equivalent weights (EEW) of the epoxy resins, and the hydroxyl equivalent weights (HEW) of the phenolic hardners are listed in Table I, together with their sources. All materials were used as received.

The ratio of epoxy resin and hardener is 1:1 based on EEW and HEW. The catalyst concentration is 1.0 phr (part per hundred resin). The detailed formulations of each samples are listed in Table II together with the material properties.

B. Preparation of Formulations

A specified quantity of catalyst was added into the epoxy resin and the mixture was stirred at around 120 °C for about one hour for a homogeneous dispersion of catalyst in the epoxy resin. Then a specified quantity of hardener was added into the mixture and stirred at 70–100 °C for 30 min. All the formulations were stored in a freezer at −40 °C. They were warmed up to room temperature prior to any evaluation. The curing conditions of all the samples were the same unless specified otherwise. The samples were placed in a convective oven and heated to 165 °C at around 5 °C/min and were continuously cured at 165 °C for 1 h. Then the samples were taken out of the oven to cool down to room temperature.

C. Characterizations

Thermal Stability of Phenolic Hardeners: A thermo-gravimetric analyzer (TGA) by TA Instruments, Model 2050 was used to investigate the weight loss of phenolic hardeners and HMPA. A sample of about 20 mg was placed in a TGA sample pan and was heated in the furnace at 10 °C/min under N_2 purge.

Material Properties of the Underfill Formulations: To study the curing profile of the formulations, a modulated differential scanning calorimeter (DSC) by TA Instruments, Model 2920 was used. A sample of about 10 mg was placed into a hermetic DSC sample pan and heated in the DSC cell at 5 °C/min to 300 °C. The onset and the peak temperatures of the exothermic diagram were recorded. The cured sample was left in the cell and cooled down to room temperature at 5 °C/min. Then the sample was reheated to 200 °C at 5 °C/min, with a temperature modulation of ±1 °C/min. The initial temperature of the heat flow step in this second thermogram is defined as the glass transition temperature (T_g) of the sample.

TABLE II
INGREDIENTS AND MATERIALS PROPERTIES OF THE UNDERFILL FORMULATIONS

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Epoxy resin	EP-A	EP-A	EP-A	EP-A	EP-B	EP-B	EP-B	EP-B	EP-C	EP-C	EP-C	EP-C	EP-D	EP-D	EP-D	EP-D	EP-A
Hardener	PH-A	PH-B	PH-C	PH-D	PH-A	PH-B	PH-C	PH-D	PH-A	PH-B	PH-C	PH-D	PH-A	PH-B	PH-C	PH-D	HMPA
Onset curing tempt (°C)	136	136	153	166	83	79	136	143	140	140	153	166	131	130	146	151	143
Peak curing tempt (°C)	155	156	167	177	154	153	171	171	161	170	168	179	151	152	159	170	163
DSC Tg (°C)	100	89	70	69	152	120	87	85	85	79	68	52	122	105	83	83	140
α1 (ppm/°C)	75	69	87	79	69	62	106	100	80	63	99	126	81	62	89	85	75
α2 (ppm/°C)	214	224	333	417	174	180	206	204	207	212	262	461	197	194	237	265	183
E' @ RT (Gpa)	2.35	2.25	2.49	2.42	3.10	3.17	2.70	2.63	2.88	2.30	2.66	1.68	2.85	2.78	2.45	2.62	2.62
E' @ Tg+40 °C (Mpa)	9.43	3.16	1.34	0.83	33.2	8.89	15.1	9.07	7.14	4.97	1.30	1.19	8.10	1.82	2.31	1.49	16.7
Viscosity @ 30 °C (Pa•s)	9.847	2.823	0.899	0.664	69.21	31.87	0.743	0.445	2.645	1.086	0.374	0.284	64.55	15.47	0.824	0.590	0.096
Moisture uptake after 100 hr	1.48	1.56	1.24	1.18	2.35	2.41	1.66	1.51	1.56	1.63	1.28	1.20	1.68	1.75	1.42	1.33	*
Die shear strength (Mpa)	55.0	64.0	47.1	34.9	51.5	59.1	57.3	56.4	75.8	59.1	47.7	34.9	73.2	78.3	61.8	53.1	**

*: Typically around 1%;

**: Very weak because of the resin crack after cure due to high internal stress.

Coefficient of thermal expansion (CTE) of a cured sample was measured on a thermo-mechanical analyzer (TMA) by TA Instruments, Model 2940. The dimension of the sample was about $5 \times 5 \times 2$ mm. The sample was heated in the TMA furnace at 5 °C/min from room temperature to 250 °C. The inflection point of the thermal expansion is defined as TMA T_g. The CTE before TMA T_g is defined as $\alpha 1$ and that after T_g as $\alpha 2$.

To study the dynamic moduli of a cured sample, a dynamic mechanical analyzer (DMA) by TA Instruments, Model 2980 was used. The sample dimension was about $18 \times 6 \times 2$ mm. The measurement was performed in a single cantilever mode under 1 Hz sinusoidal strain loading. The sample was heated at 3 °C/min in air from room temperature to 250 °C. Storage modulus (E'), loss modulus (E''), and loss angle $(\tan\delta)$ can be obtained. The peak temperature of $\tan\delta$ is defined as DMA T_g.

The study of the viscosity of the formulations was performed on a stress rheometer by TA Instruments, Model AR 1000-N. The measurement was conducted under constant shear rate of 5.0 1/s. The sample was heated from 20 °C to 120 °C at 10 °C/min.

Moisture absorption study was performed using an 85 °C/85% RH chamber. The initial weight of samples was about 1 gram and the thickness was about 2 mm. At different time intervals, the samples were taken out of the chamber and weighed. The percentage weight gain is defined as the moisture absorption at a certain time.

Adhesion of the formulations to the substrate was conducted in shear mode using a bond tester (Model 550–100 K, Royce Instruments). Samples were prepared using 2×2 mm dies with silicon nitride passivation since silicon nitride is one of the most commonly used passivation materials on the integrated circuit (IC) devices. Spherical glass beads of 75 μm diameter were added into the formulation at 0.5 wt% to ensure consistent gap size.

Flexure tests were performed using a Universial Testing Machine (UTM) by Instron. The sample dimension was about $20 \times 2.5 \times 5.0$ mm. The tests were conducted at room temperature. The loading speed was 1 mm/min. The maximum stress and the strain at break of each specimen were recorded and the flexure modulus was calculated. For each sample, around six specimens were prepared for the average as reported.

TABLE III
TEMPERATURE PROFILE OF THE REFLOW OVEN FOR FLUXING CAPABILITY TEST

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7
100 °C	150 °C	150 °C	160 °C	200 °C	220 °C	180 °C

Evaluation of Reliability of Flip-Chip on Board Packages With Underfills: The reliability of formulations #8, #10, #14, and a control sample #17 based on anhydride curing system was investigated using PB8 test chips (manufactured by Flip Chip Technology) and an FR-4 printed circuit board (PCB). The test chips and board were assembled beforehand and the samples were filled into the gap of chips and board by capillary flow after the board was preheated to 70 °C. Then the samples were cured at 165 °C for 2 h in a convective oven. The test chips were then subjected to liquid-to-liquid thermal shock (−55 °C to 125 °C, dwell time 5 min) up to 2200 cycles. The underfill fillet cracking was observed by optical microscope.

Evaluation of the Fluxing Capability of the Underfills: The fluxing capability of formulations #8, #10, and #14 was evaluated using Sn/Pb eutectic solder balls and copper foil laminated FR-4 board. The board was pre-cleaned by the following procedure: 5 min immersion in acetone, 5 min immersion in methanol, then 20 s immersion in 50/50 HCl solution, followed by DI water rinse and clean airjet drying. In the test, the solder balls were placed on the copper foil. Then a drop of the underfill formulations was applied to immerse the solder balls. The test vehicle then went through the pre-profiled seven-zone BTU reflow oven. The temperature of each zone is listed in Table III. The cross-section of the solder balls wetting on the copper foil was observed using optical microscope.

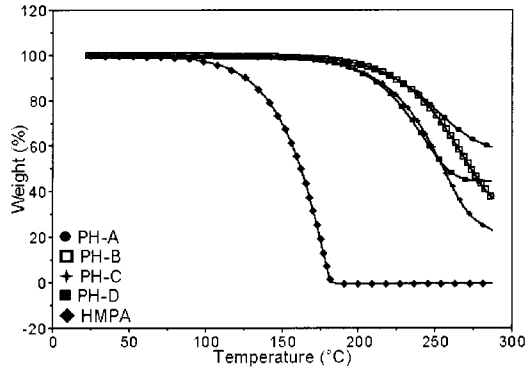


Fig. 2. Weight loss of hardeners during heating.

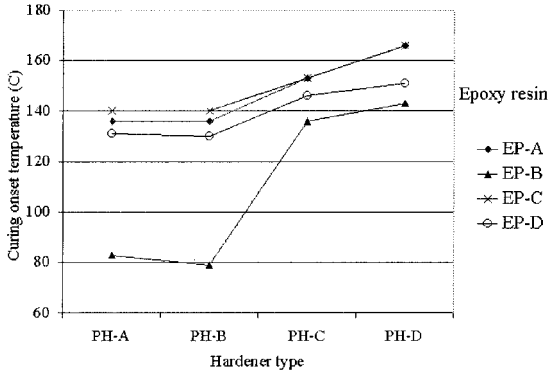


Fig. 3. Dependency of onset curing temperature on epoxy and hardener type.

III. Results and Discussion

A. Thermal Stability of Phenolic Hardener

The weight loss of the phenolic hardeners during heating is illustrated in the TGA diagrams in Fig. 2. The TGA diagram of HMPA is also listed for comparison. It is observed that since anhydride usually has a high vapor pressure, it evaporates very fast upon heating, especially under the N_2 purge. At a heating rate of 10 °C/min, the weight of HMPA dropped to zero when temperature reached 180 °C. On the other hand, the phenolic hardeners are quite stable until about 200 °C. For no-flow underfill with a latent catalyst, there should not be significant curing before the solder melts. The evaporation of anhydride during curing will cause outgassing and also will impose health threat to the environment.

B. Curing Behavior of the Underfill Formulations

The curing onset temperatures and the curing peak temperatures of all the underfill formulations are listed in Table II. Since only one catalyst at the same concentration level was investigated in this study, all the samples display similar curing peak temperatures. However, the onset temperatures showed dependence on the type of epoxy resins and curing agents. Fig. 3 shows the onset temperatures of all the underfill formulations. It can be seen that when novolac phenolic resin is used as the hardener, EP-B has a much higher reactivity than all the other epoxy resins. The reaction starts at temperatures as low as 80 °C, which makes the system inapplicable for no-flow underfill. All the other formulations possess desirable curing onset temperatures and peak temperatures for no-flow underfill applications.

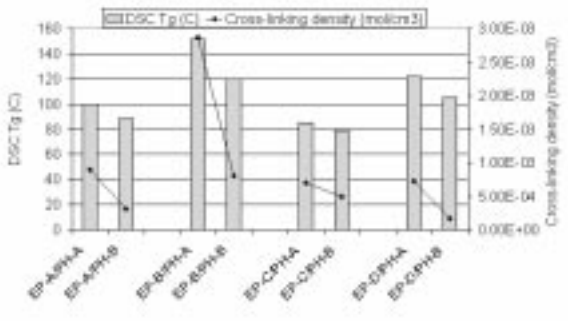


Fig. 4. Effect of crosslinking density on T_g.

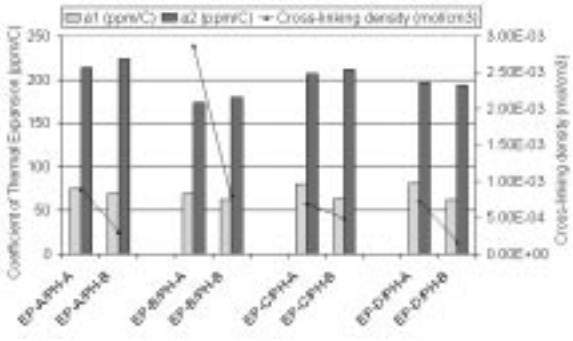


Fig. 5. Effect of crosslinking density on CTE.

It was also observed that hardeners PH-C and PH-D showed higher latency in curing reactions. The ortho-substituent on the phenol ring of PH-C and PH-D imposes a steric hindrance against the reaction. Studies have shown that the substituent not only retarded the reaction, but caused incompletely reaction between the epoxide and the phenol group as well [7]. Due to this incomplete reaction, the crosslinking density and the average molecular weight of epoxy resins cured by PH-C and PH-D are typically lower, which leads to the significant differences in material properites as discussed later.

C. Thermo-Mechanical Properties of Cured Underfills

It can be seen from the thermal mechanical properties of these formulations that all the samples have similar storage modulus at room temperature, when the polymers are in glassy state, while the storage modulus in rubbery state varies. According to the kinetic theory of rubber elasticity, the crosslinking density ρ can be determined from the storage modulus (E') in rubbery state by the following equation [8]:

$$\rho = \frac{E'}{3\phi RT}$$

in which, ϕ is a front factor which is assumed to be 1. R is the gas constant and T is the absolute temperature. Based on this theory, the crosslinking density of the samples was calculated.

Figs. 4 and 5 show the effect of crosslinking density on T_g and CTE of the epoxy resins cured by PH-A and PH-B. Disregarding the types of epoxy resins, samples cured by PH-A always have higher crosslinking density than those cured by PH-B, since PH-A has a higher functionality. It can be inferred

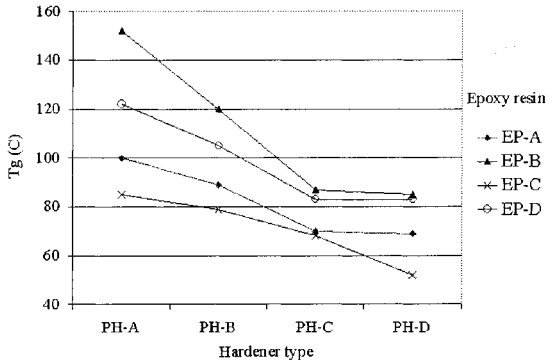


Fig. 6. Dependency of T_g on epoxy and hardener type.

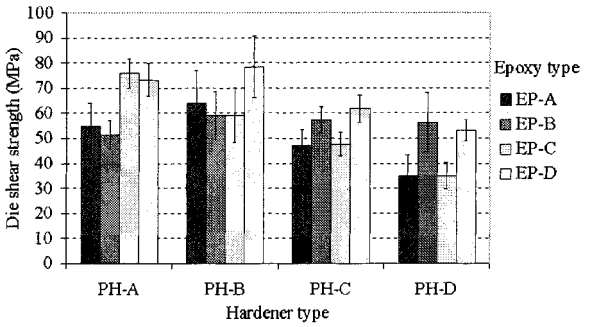
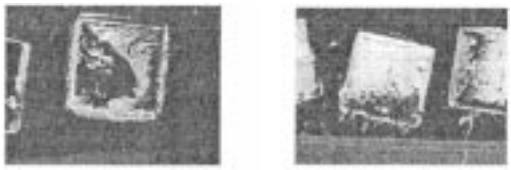


Fig. 7. Die shear strength toward silicon nitride passivation.



(a) (b)

Fig. 8. Fracture surfaces in die shear test: (a) EP-C/PH-A and (b) EP-D/PH-C.

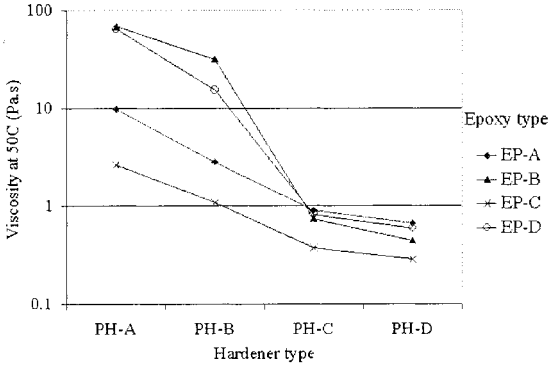


Fig. 9. Dependency of viscosity on epoxy and hardener type.

that higher crosslinking density leads to higher T_g. Samples with higher crosslinking density usually have higher $\alpha 1$ but lower $\alpha 2$. Results of epoxy resins cured by PH-C and Ph-D show the same trend. This confirms the relationship between crosslinking density and physical properties observed by Ogata *et al.* from epoxy molding compound [9]. They showed that the crosslinking density is related to the free volume in the cured epoxy resins and is the most dominant factor that determines various physical properties of the resins. When the thermosetting material cools down from high temperature after cure, the high crosslinking density would restrict the mobility of molecules. So it goes through a glass transition at a high temperature. Less efficient packing caused by crosslinking would introduce more free volume in the system, resulting in a high CTE below T_g. Beyond T_g, since the high crosslinking prevent the molecules to move freely, CTE is lower than that of samples with low crosslinking density.

The chemical nature of the polymer is also of critical importance to material properties of the cured resin. Fig. 6 shows clearly that there are strong dependence of glass transition temperature on the types of epoxy resins and hardeners. According to Fig. 3, EP-A, EP-C, and EP-D showed similar curing behavior. When the same hardener is used, the cured resin also have comparable crosslinking density (see Figs. 4 and 5). However, the glass transition temperature of EP-D resins is consistently higher than that of EP-A and EP-C. The naphthalene ring structure in EP-D gives rise to its rigidity of the chains and restricts the mobility. It is also observed that resins cured with hardeners PH-C and PH-D tend to give poor thermo-mechanical properties (low T_g and high CTE), compared with the resins cured with PH-A and PH-B. As mentioned early, the incomplete reaction caused by steric hinderance of the ortho-substituent might lead to a low average molecular weight of the resin after curing. The excess of chain ends contributes to the free volume in the resin, which causes low T_g and high CTE. On the other hand, the ortho-substituent on the phenol ring also may lead to inefficient packing, resulting in a low T_g and high CTE.

D. Adhesion of Underfill Toward Die Passivation

From the die shear strength data shown in Table II, it can be concluded that compared with the general anhydride cured epoxy resins, whose adhesion strength toward silicon nitride is typically around 50 Mpa, the adhesion of phenolic curing system is higher. Fig. 7 shows the die shear strength of underfill toward silicon nitride passivation of all the underfill formulations. In those samples with relative low adhesion, bulk failure was observed during die shear test. Fig. 8 shows the examples of fracture surfaces in die shear test. The fracture surface in (a) indicates an adhesive failure while that in (b) indicates a cohesive failure. The results suggest that epoxy resins cured with phenolic resin have very high interfacial adhesion toward silicon nitride.

E. Reological Behavior of Underfill Formulations

The viscosity of most base formulations is much higher than that of the anhydride-containing one. Especially, those formulations with PH-A and PH-B as the hardener are solids or semi-solids at room temperature. Fig. 9 shows the viscosity of the underfill formulations at 50 °C when different epoxy resins and hardeners are used. It can be seen that the formulations with EP-C have the lowest viscosity although EP-B by itself has lower viscosity than EP-C. Since EP-B is more reactive, the reaction between epoxy and hardener might start at low temperatures, which gives rise to the high viscosity of the formulations with EP-B. In terms of material properties of cured resins, hardeners PH-A and PH-B are more desirable.

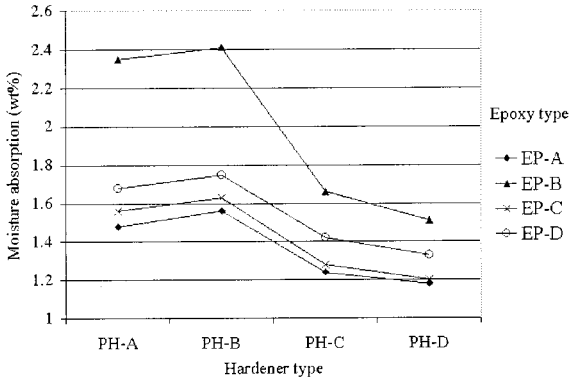


Fig. 10. Moisture absorption of underfills after 100 h in 85/85 aging.

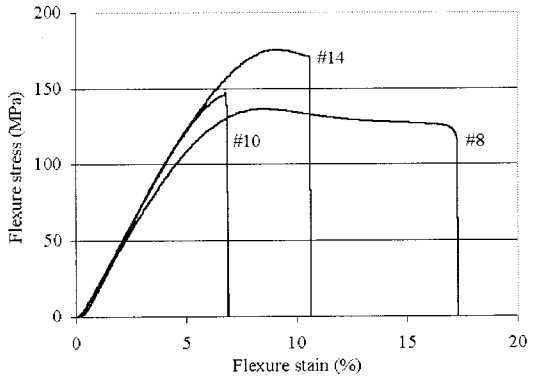


Fig. 11. Stress–strain curve of the three samples in the flexure test.

However, the high viscosity might limit their application in no-flow underfill.

F. Moisture Absorption During 85 °C/85% RH Aging

The moisture uptake data during 85°C/85% RH aging is also included in Table II. All formulations showed saturation in moisture uptake after 100 h exposure in 85 °C/85% RH chamber. Fig. 10 shows the saturated moisture absorption of all formulations. It is observed that epoxy EP-B has the highest moisture uptake in the aging test probably due to two facts. First, the trifunctional epoxy greatly increases the crosslinking density of the cured resin and the high free volume in glassy state caused by less efficient packing induces high moisture uptake. Second, the presence of N atom introduces high polar site on the structure of the resin, which leads to high moisture uptake as well.

G. Flexure Test

Flexure test was performed using three samples, #8, #10, and #14. The typical stress–strain curve of the three samples are shown in Fig. 11. It can be seen that sample #8 differs from samples #10 and #14 in that it showed a ductile failure in the flexure test. The strain at break is much higher than that of the other two samples. However, the yield stress is lower in sample #8. In Fig. 12, the maximum stress, strain at break and flexure modulus of the three samples are compared.

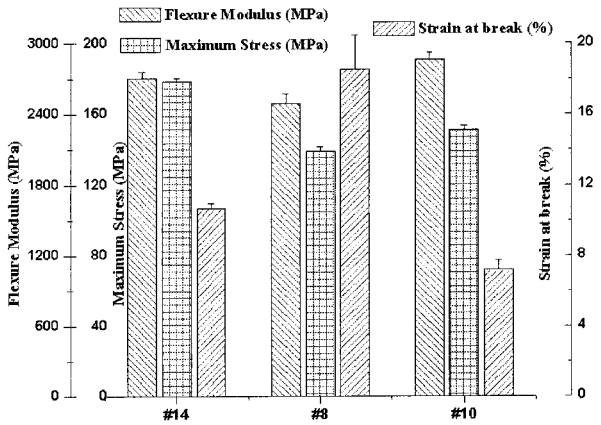


Fig. 12. Maximum stress, flexure modulus, and strain at break of the three samples in flexure test.

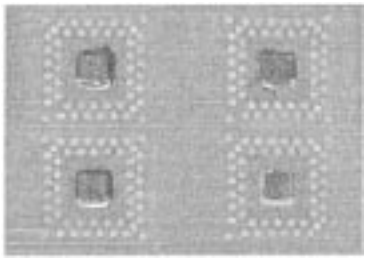


Fig. 13. Assembly for reliability test.

TABLE IV
RELIABILITY OF BASE FORMULATIONS

Sample No.	Solder joint reliability	Fillet cracking
# 8	600 cycles	700 cycles
# 10	> 2200 cycles	> 2200 cycles
# 14	1900 cycles	1800 cycles
# 17	400 cycles	100 cycles

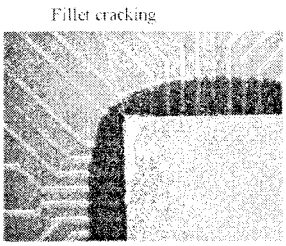


Fig. 14. Underfill fillet cracking observed in the thermal shock test.

H. Evaluation of Reliability of Underfill Formulations

Fig. 13 shows the assembly used to evaluate the reliability of formulations #8, #10, #14, and a control sample of anhydride cured underfill #17. Table IV lists the reliability of the solder joints of each chip and the start time of underfill fillet cracking. Fig. 14 shows the underfill fillet cracking of sample 8 after 700 cycles. It can be seen that the underfills in the assemblies that failed early tended to show fillet cracking during the early stage

(a) (b) (c)

Fig. 15. Cross sections of solder balls wetting on copper with the underfill: (a) #8; (b) #10; and (c) #14.

of thermal shock. Formulations 10 and 14 showed very high solder joint reliability. Neither of them had any fillet cracking until late stage of thermal shock, which indicates high fracture toughness of the material.

The investigation of the material properties has shown that formulations #10 and #14 are featured by low CTE and high adhesion. The glass transition temperatures of these two samples are moderate, suggesting that high T_g of underfill material is not critical to the reliability. Instead, it might result in a higher residue stress in underfill after cure to begin with, which increases the probability of cracking during the thermal shock test. Compared with nonanhydride formulations, sample 17, which is based on epoxy/anhydride system, is characterized with high glass transition temperature, high modulus and high crosslinking density. However, the reliability performance of the assembly with sample 17 was poorer than that of the nonanhydride formulations. Note that this sample showed early fillet cracking during the thermal shock test. The high internal stress introduced in curing and the brittle natural of underfill might be the main reasons for its early failure.

I. Evaluation of Fluxing Capability of the Underfills

Two basic requirements for no-flow underfills are curing latency to allow the solders to wet the contact pads before the underfill gels, and the fluxing capability to eliminate the metal oxides and to faciliate the wetting of solders on the pads. The simple wetting test of solder balls on the copper laminated FR-4 board provides an evaluation of the feasibility of no-flow process. The wetting of solder balls on the copper using underfills #8, #10, and #14 was observed in the cross-sections shown in Fig. 15. Results indicate that all three formulations provide sufficient fluxing capability for eutectic Sn/Pb solder to wet on the copper pad. Unlike the usual no-flow underfill in which external fluxing agents need to be incorporated into the underfill formulation, phenolic resin itself with an active proton can provide the fluxing capablity necessary for no-flow process. This self-fluxing capability not only simplifies the procedure of preparing the underfill formulation, but also eliminates problems that might arise from the possible underfill/flux incompatibility. The wetting capability of these three underfills toward lead-free solder was also conducted in an effort to develop nonanhydride no-flow underfill for lead-free bumped flip-chip applications. However, the results showed that the underfills cured before the melting of the Sn/Ag/Cu alloy solder balls since the melting point of this alloy is higher than that of the eutectic Pb/Sn. Further work is carrying out to search for a catalyst with higher curing latency for epoxy/phenolic system.

IV. Conclusions

Phenolic resins were investigated as the hardeners for epoxy resins in the application of no-flow underfill. The material properties of epoxy resins cured with different phenolic hardeners were studied. The results showed that the crosslinking density and the chemical nature of the polymer are two dominant factors that determine various physical properties of the cured resins. For resins with similar chemical structure, higher crosslinking density leads to higher T_g, higher CTE before T_g, but lower CTE after T_g. It was also observed that resins cured by PH-A and PH-B have higher T_g and lower CTE than those cured by PH-C and PH-D when the same epoxy resins are used. This relates to incomplete reaction of PH-C and PH-D and the insufficient packing caused by ortho-substitute group on the chain.

Thermal shock test of the flip-chip on board packaging with underfills showed that the solder joint reliability is closely related to the underfill cracking behavior. For high reliability, low CTE, high fracture toughness and high adhesion of underfill is desirable. The assembly with nonanhydride base formulation has passed 2200 cycles of thermal shock test. Solder wetting test showed that pheonolic resins can provide sufficient self-fluxing capability for eutectic Sn/Pb solder to wet on copper. The epoxy/phenolic system has a great potential for a highly reliable and environmental friendly no-flow underfill process.

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